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Nonlinear Dynamics and Nucleation Kinetics in Near-Critical Liquids

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The objective of our study is to model the non-linear behavior of a near-critical liquid following a rapid change of the temperature and/or other thermodynamic parameters (pressure, external electric or gravitational field). The thermodynamic critical point is manifested by large, strongly correlated fluctuations of the order parameter (particle density in liquid-gas systems, concentration in binary solutions¹⁻³) in the critical range of scales. The largest critical length scale is the correlation radius r_c . According to the scaling theory, r_c increases as $r_c = r_0 \epsilon^{-\alpha}$ when the non-dimensional distance $\epsilon = (T - T_c)/T_c$ to the critical point decreases. Here, T_c is the critical temperature, and the critical exponent α is $\approx 2/3$. The relaxation time $\tau(r_c)$ of fluctuations on the correlation radius length scale may be estimated near T_c as $\tau(r_c) = \tau_0 \epsilon^{-(3\nu+z)}$, where the microscopic time τ_0 is about 10^{-13} sec, and the numerical value of the related critical exponent is approximately $3\nu+z \approx 2$.

The normal gravity alters the nature of correlated long-range fluctuations when one reaches $\epsilon \sim 10^{-5}$, and correspondingly $\tau(r_c) \sim 10^{-3}$ seconds; this time is short when compared to the typical experimental time. In microgravity conditions, one may study a statistically homogeneous critical liquid which is orders of magnitude closer to T_c than that in a ground-based experiment. Recently, the ZENO experiment¹ has set a benchmark $\epsilon \sim 10^{-7}-10^{-8}$, $r_c \sim 1-10 \mu\text{m}$, and $\tau(r_c) \sim 10^1-10^3$ s. This achievement manifests a qualitative change of the physical situation: that close to the critical point, the life-time of long-range fluctuations exceeds the typical experimental time-scale of seconds and minutes, and one is able to experimentally study the nonequilibrium, transient and steady, states of the material. On the other hand, in microgravity experiments conducted very close to the critical point a speeded-up equilibration may result in a long-living non-equilibrium state in some parts of the liquid. A theoretical model for the kinetics of those states is then needed to interpret the experimental data.

Close to the critical point, a rapid, relatively small temperature change $\delta T \ll T_c$ may perturb the thermodynamic equilibrium on many length scales. The critical fluctuations have a hierarchical structure, and the relaxation involves many length and time scales. Due to fragility of the near-critical equilibrium, the response of the system to such a perturbation is nonlinear one, and non-linearity plays the main role in the relaxation kinetics.

Above the critical point, in the one-phase region, we consider the relaxation of the liquid following a sudden temperature change that simultaneously violates the equilibrium on many scales. Below T_c , a non-equilibrium state may include a distribution of small scale phase droplets (clusters of one phase in the matrix of the other one); we consider the relaxation of such a droplet following a temperature change that has made the phase of the matrix stable.

The transient near-critical states created by a rapid temperature change differ in important details from those studied in the equilibrium scaling theory and the dynamic renormalization group (DRG). The application of the DRG to the new situation assumes an extension of scaling hypothesis. We give physical arguments in favor of the proposed scenario of the hierarchical relaxation. The theory predicts new scaling laws for the large-time dependence of the temperature and for statistical characteristics of long-range fluctuations. These predictions may be tested by light

scattering experiments and by direct visualization techniques. An experimental test of the predictions will check the suggested scenario and the enhanced scaling hypothesis.

The following physical situations are considered.

1. A step away from the critical point where a large range of critical fluctuations disappears.
2. A step towards the critical point where a new range of strongly interacting fluctuations appear.
3. A phase droplet (nucleus) in a matrix of the other phase under varying conditions of the matrix stability.
4. The nucleation of FCC (face centered cubic) clusters following a deep quench of a computer-generated "liquid".

We start with a Langevin-type description of the system. The atomic scale fluctuations are assumed to play the role of a "thermal bath" for the larger scale degrees of freedom. At times $t > \tau_0$ one characterizes this "thermal bath" by a time-dependent temperature $T(t)$. The time τ_{ch} of the rapid temperature change δT is large when compared to τ_0 , but small when compared to the relaxation time on large scales $r \gg r_0$: $\tau(r) > \tau_{ch} > \tau_0$. On the macroscopic time-scales, one considers a sharp temperature step at $t=0$. The mathematical model is as follows. To study the fluctuations of the order parameter (particle density in the liquid-gas system), one represents the order parameter field $\phi(\mathbf{r}, t)$ in the form¹⁻³

$$\phi(\mathbf{r}, t) = \sum_{\mathbf{k}=0}^{k_\lambda} \phi_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{r}} ; \quad (1)$$

the variable cut-off length $\lambda=1/k_\lambda$ is introduced in (1) following the Wilson-Kadanoff renormalization group (RG) method^{2,3}. The probability $W_{eq,\lambda}(\phi)D\phi(\mathbf{r})$ to find the equilibrium system in an element $D\phi$ of the configuration space defines the effective Hamiltonian H_λ ^{1,2}:

$$W_{eq,\lambda}(\phi)D\phi = \exp\left(\frac{F_\lambda - H_\lambda(\phi)}{k_b T_c}\right) D\phi, \quad F_\lambda = -k_b T_c \ln \int \exp\left(-\frac{H_\lambda}{k_b T_c}\right) D\phi, \quad (2)$$

$$H_\lambda = -F_{reg} - k_b T_c \ln \sum_{(\phi(r))} \exp\left(-\frac{H^{(mic)}}{k_b T_c}\right), \quad F_{reg} = F - F_\lambda.$$

In the definition (2), $H^{(mic)}$ is the microscopic Hamiltonian of the system, k_b is the Boltzmann constant, F is the equilibrium free energy of the system, F_λ and F_{reg} are the singular and the regular parts of the free energy respectively². The sum in (2) is over all states of the system with $\phi(\mathbf{r})$ a given function. The field $\phi(\mathbf{r})$ defined by (1) represents only a small fraction of the degrees of freedom of the system, most of which belong to small length scales $r < \lambda$. The effective Hamiltonian $H_\lambda(\phi, \epsilon)$ is defined as an average over these small scale degrees of freedom. Up to a regular function of ϵ , $H_\lambda(\phi, \epsilon)$ is the free energy of the system in the equilibrium state with a given configuration of the large scale field $\phi(\mathbf{r})$.

The fluctuations of the conserved order parameter $\phi(\mathbf{r}, t)$ are described by the Langevin equation of the form

$$\frac{\partial \phi}{\partial t} = -\Delta \Gamma_\lambda \left(-\frac{\delta H_\lambda}{\delta \phi} + f_{\lambda, ext} \right). \quad (3)$$

Here, Γ is the (conserving) kinetic coefficient. The extraneous random force $f_{ext}(\mathbf{r}, t)$ models the

interaction of the order parameter with small-scale degrees of freedom of the system. The kinetic coefficient Γ_λ and the effective Hamiltonian H_λ are dependent on the cut-off length λ as described by the dynamic renormalization group (DRG). An essential condition of applicability of the method is the thermal equilibrium at length-scales $R < \lambda$; the thermodynamic equilibrium at scales larger than λ is not required by the renormalization group method, the relaxation on these scales is described by the equations of the theory. In the course of relaxation, the fluctuations on scales $R > \lambda$ are non-equilibrium and exchange energy with smaller scales. One has to study separately a step towards the critical point ($r_{c,fin} \gg r_{c,in}$) in which a new range of strongly interacting fluctuations appear, and a step away from the critical point ($r_{c,fin} \ll r_{c,in}$) where a large range of critical fluctuations disappears. Here and below, the subscripts $_{fin}$ and $_{in}$ label the characteristics of the final and the initial ($t < 0$) states of the system.

For a large temperature change away from the critical point, $r_{c,fin} \ll r_{c,in}$. Most important changes in the fluctuation picture are expected in the range of scales $r_{c,fin} < r < r_{c,in}$. In systems characterized by a conserved order parameter, the relaxation on small length-scales takes less time than on the large ones. At a given time t , the fluctuations on length-scales $r < \lambda_{eq}(t)$ have approached the new equilibrium state while the larger scale fluctuations are still non-equilibrium. Here, $\lambda_{eq}(t)$ is the equilibration length increasing with increasing time. At large $t > \tau(r_{c,fin})$, $\lambda_{eq}(t)$ exceeds the correlation radius $r_{c,fin}$ of the final equilibrium state. We apply the DRG to find the effective Hamiltonian on large scales $r > r_{c,fin}$, $t > \tau(r_{c,fin})$ in the form

$$H_\lambda = \sum_{k < \lambda} H_k, \quad H_k = \frac{1}{2\chi_{fin}} |\phi_k|^2. \quad (4)$$

Here, $\chi_{fin} \equiv \chi(\epsilon_{fin}) \sim \epsilon_{fin}^{-\nu(2-\eta)}$ is the susceptibility of the system in the final state (the isothermal compressibility for the liquid-gas system). The free field form of the resulting Hamiltonian means that at $t > \tau(r_{c,fin})$ the temperature shift switches off the interaction in the range of scales $r > r_{c,fin}$. The relaxation of the long-range configuration to the final equilibrium state follows the laws of the free field kinetics. For the time-dependent average $M_k(t) = \langle |\phi_k(t)|^2 \rangle$ one obtains

$$M_k(t) = (M_{k,in} - M_{k,fin}) e^{-\frac{t}{\tau_k}} + M_{k,fin}, \quad (5)$$

$$M_{k,in} = \langle |\phi_k|^2 \rangle_{in}, \quad M_{k,fin} = 2k_b T_c \chi_{fin}; \quad \tau_k = \frac{1}{D_{fin} k^2}.$$

The diffusion coefficient D_{fin} is scale-independent at the length scales $\lambda \gg r_{c,fin}$. We have also studied the shape relaxation of probability distribution function of long-range fluctuations.

A rapid temperature increase requires more energy than a gradual heating. At large times, the excess energy is gradually released; in a system adiabatically insulated at $t > \tau(r_{in})$, the energy release raises the temperature of the system. The scaling law for the large-time temperature "tail" has the form

$$\epsilon(t) - \epsilon_{fin} \sim \epsilon_{fin} [\tau(r_{c,fin})/t]^\zeta; \quad \zeta = (1 + \eta)/2. \quad (6)$$

Here, $\eta \approx 0.033$ is the critical exponent of the order parameter.

Let us now consider a step toward the critical point: $\epsilon_{in} \gg \epsilon_{fin}$. In contrast to the above case,

the harmonics ϕ_k in the range $r_{c,in} < 1/k < r_{c,fin}$ strongly correlate in the final state, and the problem cannot be reduced to that of a single harmonic. The suggested scenario is sequential equilibration: at a given time t , the fluctuations on small scales up to a time-dependent equilibration length scale $\lambda_{eq}(t)$ will equilibrate while the harmonics ϕ_k with $k < 1/\lambda_{eq}$ will retain the initial magnitudes. These magnitudes are small compared to the final ones, and may be neglected. The statistics and the kinetics of the fluctuations on scales $r < \lambda_{eq}(t)$ yield then the equilibrium scaling relations^{2,3,4}: on a scale $\lambda < \lambda_{eq}(t)$ the relaxation time is $\tau(\lambda) \sim \lambda^2/D(\lambda) \sim \lambda^{3+z/\nu}$, where z is the critical exponent for the viscosity^{2,4}. The time dependence of λ_{eq} is controlled by the condition that $\tau(r) < t$ for $r < \lambda_{eq}(t)$, and $\tau(r) > t$ for $r > \lambda_{eq}(t)$. The scale $\lambda_{eq}(t)$ has then the equilibration time $\tau(\lambda_{eq}(t)) \sim t$; this relation gives the scaling law for $\lambda_{eq}(t)$.

$$\lambda_{eq}(t) = r_{in} [t/\tau(r_{in})]^p, \quad p = \frac{\nu}{3\nu + z}. \quad (7)$$

The theoretical values (see ref.⁵) $\nu = 0.630$ and $z = 0.063$ give $p = 0.32$.

The sequential "cooling" of large scale fluctuations is accompanied by release of heat $Q(t)$. The heat released on the scale λ_{eq} is transferred to smaller scales and through the small scale "heat bath" to the thermostat that maintains the temperature $T(t)$. In a system that is adiabatically insulated during relaxation, the heat transferred from the large scales to the smaller ones will result in an increase in the temperature $T(t)$. A rapid cooling results then in a temperature minimum. The scaling law for the large time "tail" in reduced temperature is

$$\epsilon(t) \propto \epsilon_1 [\tau(r_{c,in})/t]^\zeta, \quad \zeta = 1/(3\nu + z). \quad (8)$$

The critical exponent $\zeta = 1/(3\nu + z)$ differs from ζ_+ given by (6). Using the approximate theoretical values for the critical exponents (see ref.⁵), one obtains for the liquid-gas and for the binary mixtures critical points $\zeta_+ \approx 0.517$ and $\zeta_- \approx 0.512$. Both exponents are surprisingly close to each other and to the mean-field value $1/2$.

Below the critical temperature, there are two phases of the material, one of which is metastable except for the phase transition line. A non-equilibrium state may include droplets of one phase in the matrix of the other one. In the literature, this was studied for the case of a metastable matrix state, when the droplet is a nucleus of the new, stable, phase. We have considered a more general case when the embedding matrix may be metastable or stable. In the vicinity of a phase equilibrium line limited by the spinodals, the non-linearity of the equations for the two-phase system results in a finite width of the interface separating the droplet from the matrix. On both sides of the binodal, the droplet may be characterized by a critical radius; when the matrix is in the stable phase, the critical radius becomes negative. The nucleus then is always subcritical and decays with time. By changing the thermodynamic stability of the matrix, one is able to control the growth and decay of the nucleus. Outside the part of the thermodynamic plane separated by the spinodals of both phases, the relaxation of the droplet leads to the broadening of the boundary. Asymptotically, the profile of the order parameter tends to a Gaussian one, with the width $R(t)$ growing according to the diffusion law $R^2 \sim t$.

The growth of small nuclei of the cubic central faced crystalline phase following a deep temperature quench to the liquid state spinodal was observed in a computer-generated "liquid". To discriminate clusters having the FCC local order, the statistical theory of pattern recognition was

applied. The method proposed allows one to compare nucleation kinetics in real and in simulated systems.

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The results of this study were published in the following papers:

1. A. Z. Patashinski, "Rapid temperature changes in near-critical systems", to appear in *Physics Letters*.
2. A. Z. Patashinski, "A temperature step away from a critical point", submitted to *Phys.Rev.E*.
3. A. Z. Patashinski, "A phase droplet near the phase transition line", submitted to *J.of Chem. Phys.*
4. A. C. Mitus, F. Smolej, H. Hahn, and A. Z. Patashinski, "Theory and practice of shape spectroscopy of local FCC structures in computer simulations of nucleation and crystallization", to appear in *J.of Physics*.
5. A. C. Mitus, F. Smollay, H. Hahn, and A. Z. Patashinski, "Q₄₅₅-spectroscopy of shapes and FCC-nucleation in a Lennard-Johnes system", *Europhysics Letters*, **32**(9), 777 (1995).

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